

Electrochemical Study of α -Hydroxy-Anilinebenzoquinones Derivatives in Acetonitrile. Reduction Mechanism Control by both Acidity Level of Electrolytic Medium and Structural Modifications.

J. A. Bautista-Martínez¹, G. Cuevas², N. Macías-Ruvalcaba¹, I. González³ and M. Aguilar-Martínez¹.

Universidad Nacional Autónoma de México. Facultad de Química¹ e Instituto de Química². Ciudad Universitaria, 04510, México D.F., MÉXICO. and ³Universidad Autónoma Metropolitana-Iztapalapa, Departamento de Química, Apartado postal 55-534, 09340 México D.F., MÉXICO.

The electrochemical study in acetonitrile of perezone (2-(1,5-dimethyl-4-hexenyl)-3-hydroxy-5-methyl-1,4-benzoquinone, figure 1, $R_1=R_2=H$) and 11 anilinederivatives (figure 1) was carried out in order to determine the effect of different experimental conditions on the electroreduction mechanisms.

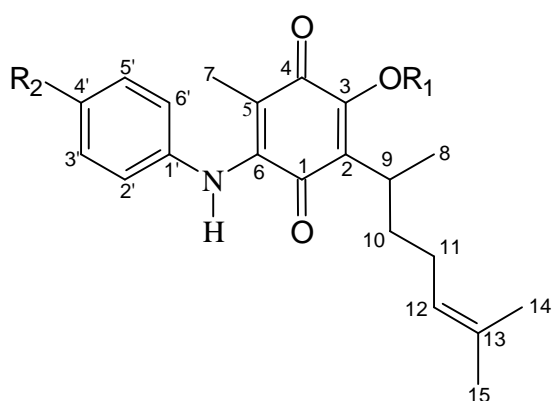


Figure 1. Structure of (2-(1,5-dimethyl-4-hexenyl)-3-hydroxy-5-methyl-6-(R_2 -phenyl)amine-1,4-benzoquinone (APZs) and their 3-methoxy derivatives ($R_1=Me$, APZMs synthesized in this work).

The effect of a hydrogen bond between the α -hydroxy ($R_1=H$, figure 1) and the carbonyl $C_4=O_4$ group was determined in the perezone derivatives, substituted by electron-donors and electron-withdrawing groups (R_2) such as $-OMe$, $-Me$, $-Br$ and $-CN$, by comparing the $-OH$ (APZs, $R_1=H$) with the $-OMe$ (APZms, $R_1=CH_3$) derivatives.¹ The typical behaviour of quinones in the aprotic medium² was not observed for APZs (figure 2a) due to the presence of coupled self-protonation reactions. The self-protonation process gives rise to a first wave (I'_c), which corresponds to an irreversible reaction of quinone (HQ) reduction to hydroquinone (HQH_2), and to a second electron transfer (II'_c) due to the reversible reduction of perezonate ($Q^-/Q^{\bullet-}$) formed during the self-protonation process. To control the chemical coupled reaction, in the present work, three pathways were considered: the methylation of the $-OH$ group (APZms, $R_1=CH_3$), the addition of a basic reagent (weak or strong), to deprotonate the APZs and the addition of proton donors (weak or strong). The first case led to the recovering of the reversible bielectronic behaviour (figure 2b), indicating the non-acidic properties of the N-H group.

For the second case, in the presence of a strong base (phenolate), important changes in the reduction process were observed. Only the reduction of perezonate (Q^-) obtained from the acid-base reaction of APZs with a strong base gave rise to the dianion-radical ($Q^{\bullet-}$)(figure3b).

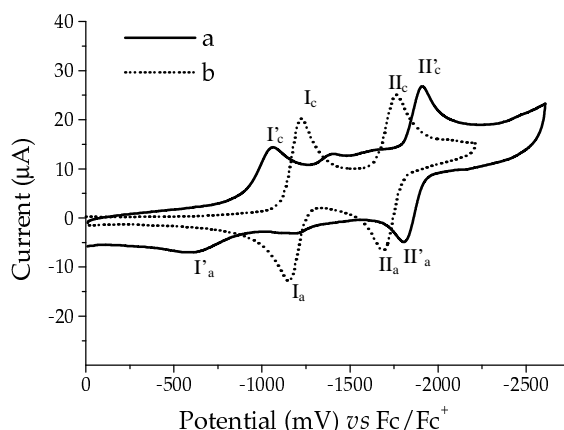


Figure 2. Typical cyclic voltammograms obtained in glassy carbon electrode (7mm²), scan rate 100 mVs⁻¹ in 0.1 M Et₄NBF₄/acetonitrile in the presence of the corresponding quinone 1 mM a) *p*-MeAPZ and b) *p*-MeAPZm. The cathodic (I_c , II_c and I'_c , II'_c) and anodic (I_a , II_a and I'_a , II'_a) peaks are indicated in the figure.

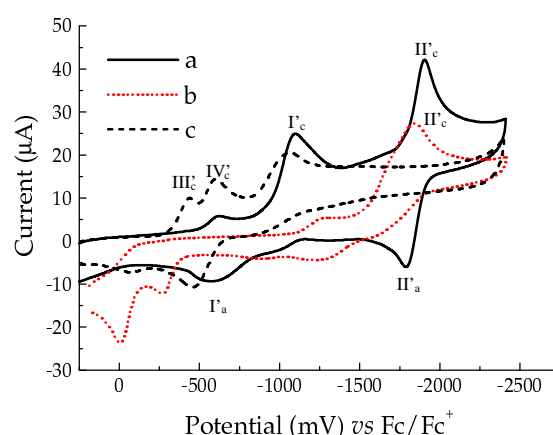


Figure3. Typical cyclic voltammograms obtained in glassy carbon electrode (7mm²) scan rate 100 mVs⁻¹ in 0.1M Et₄NBF₄/acetonitrile of 1mM *p*-MeOAPZ a) in the absence of basic or acidity additives b) in the presence of 2mM Me₄N⁺C₆H₅O⁻ c) in the presence of 0,6 mM of HClO₄.

In the last case, the presence of a weak acid produced a stoichiometry change in the reduction process. With the addition of a strong acid some waves corresponding to the reduction of protonated species, prior to the electron transfer process, were observed (figure3c).³ A linear variation in the cathodic peak potentials (E_{pc}) vs Hammett σ_p constants, associated with the different electrochemical transformations, were obtained: either $Q/Q^{\bullet-}$, $Q^{\bullet-}/Q^{2-}$ for APZms or HQ/HQH_2 and $Q^-/Q^{\bullet-}$ for APZs confirmed the substituent effect on the electroreduction of these molecules.

Acknowledgments. We are grateful to Consejo Nacional de Ciencia y Tecnología (CONACyT) for the financial support given via grant No. 28016-E and for fellowships to NMR and JABM, who are also grateful to DGEP for a complementary fellowship.

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